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(71)Applicant : TEIJIN CHEM LTD

(72)Inventor : YANAGIDA TAKATSUNE
TAKEYA YUTAKA

(54) PRODUCTION OF BROMINATED POLYSTYRENE PARTICULATE

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a brominated polystyrene particulate having a low residual solvent content by a simple and easy process while saving resources and energy by dissolving brominated polystyrene prepared by brominating polystyrene having a specified number average mol.wt. in a halogenous organic solvent, heating the resultant solution in a heating zone and jetting the solution out of the heating zone into a low pressure zone wherein the pressure is lower than in the heating zone to cause the flash evaporation of the solvent.

SOLUTION: A brominated polystyrene obtained by brominating polystyrene having a number average mol.wt. of 10,000-500,000 and preferably a mol.wt. distribution of 1.0-3.0 is dissolved in a halogenous organic solvent preferably having a normal-pressure b.p. of 20-90°C to give a solution preferably having a concentration of 5-40 wt.%. After heated in a heating zone, the solution is jetted out of the heating zone into a low pressure zone wherein the pressure is lower than in the heating zone to cause the flash evaporation of the solvent. In the heating zone, a long and narrow pipe through which the solution flows is heated from the outside by a heating medium. The pressure difference between the heating zone and the low pressure zone is preferably 3 kg/cm2 or higher. When the solution is jetted out of the heating zone, the temperature of the solution is preferably not lower than the b.p. of the solvent.

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* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] The manufacture approach of the bromination polystyrene particulate matter characterized by making the low reduced pressure region of a pressure blow off from this heating region, and carrying out flash vaporization of this organic solvent after heating the halogen system organic solvent solution of bromination polystyrene with which number average molecular weight brominated the polystyrene of 10,000-500,000, and was obtained in a heating region.
[Claim 2] A halogen system organic solvent is the manufacture approach of the bromination polystyrene particulate matter according to claim 1 which is the range the ordinary pressure boiling point of whose is 20 degrees C - 90 degrees C.
[Claim 3] The manufacture approach of a bromination polystyrene particulate matter according to claim 1 that the concentration of the halogen system organic solvent solution of bromination polystyrene is 5 - 40 % of the weight.
[Claim 4] The manufacture approach of a bromination polystyrene particulate matter according to claim 1 that a heating region is the method which heats from the exterior long and slender tubing with which the halogen system organic solvent solution of bromination polystyrene leads with a heat carrier.
[Claim 5] The manufacture approach of a bromination polystyrene particulate matter according to claim 1 that the differential pressure of a heating region and a reduced pressure region is 3kg/cm2 or more.

[Translation done.]

flash vaporization of the volatile component is carried out. Tubing with it uses, the feed hopper and the other end to which that end supplies a bromination polystyrene solution quantitatively are the outlet which carries out opening to the reduced-pressure region held to the pressure lower than a heating region, and warm water, a heat carrier, for example, a steam, with this long and slender tubing suitable from the outside, a thermal oil, etc. are preferably heated by the steam. [the long and slender desirable for example, heating region heated with a heat carrier from the exterior although the heating apparatus of arbitration is used in order to heat a bromination polystyrene solution in a heating region, and] [long and slender]

[0013] Within tubing, a volatile component reaches by indirect heating at the boiling point, the bromination polystyrene solution supplied quantitatively and continuously from the feed hopper evaporates, and air bubbles generate it. Since the steamy volume is very large as compared with the volume of a solvent when evaporation of a halogen system organic solvent starts, the rate of flow increases rapidly and efficiency of heat transfer becomes size remarkably. The second half in this tubing, it will be evaporated and overheated by most solvents, and bromination polystyrene will be in the solid condition which contains a solvent only about several%. The solvent in the bromination polystyrene of a solid condition evaporates further, and the amount of residual solvents in the bromination polystyrene particulate matter obtained as a result becomes a low value at the same time it carries out the flash plate of the solvent which blew off in the reduced pressure region in this condition. Moreover, the solvent steam separated from the bromination polystyrene solution is made to condense by indirect cooling by a capacitor etc., and are collected easily. In addition, it is preferably [as for the temperature of the bromination polystyrene solution at the time of making it blow off from a heating region, it is desirable that it is the temperature more than the boiling point of the organic solvent in the area within heating, and / although there should just be differential pressure of a heating region and a reduced pressure region more than extent in which the solvent in a bromination polystyrene solution carries out a flash plate] desirable more preferably to make it 5-30kg/cm2 still more preferably 3-30kg/cm2 3kg/cm2 or more.

[0014] corning the bromination polystyrene particulate matter obtained in this way with a roll type compression granulating machine etc. -- the shape of a granule -- or it can also be made the shape of powder by grinding.

[0015] In this invention, after heating the halogen system organic solvent solution of the bromination polystyrene which brominated the polystyrene which has specific number average molecular weight, and was obtained, the bromination polystyrene particulate matter which is made to carry out flash vaporization of this organic solvent, and is obtained is excellent in thermal stability with a good hue with high bromine content.

[0016] A hue dissolves 0.10g of samples in a 50ml methylene chloride, and can evaluate this solution by the value (APHA) measured as compared with a HAZEN standard color solution, the bromine content of the above-mentioned bromination polystyrene has 65 - 68% of the weight of the desirable range, and 15 or less are [as for the value of this APHA, 20 or less are desirable, and] more desirable.

[0017] As for the above-mentioned bromination polystyrene, it is desirable that the amount of inorganic bromines generated when it heats for 10 minutes at 320 degrees C is 300 ppm or less, 1 ppm - its 300 ppm are more desirable, and its 1-290 ppm are still more desirable. The hue of bromination polystyrene is good in the amount of inorganic bromines being 300 ppm or less, and it excels in thermal stability and is desirable. The amount of inorganic bromines heats bromination polystyrene for 10 minutes at 320 degrees C under a nitrogen air current here, the trap of the part for the inorganic halogen in the gas which occurred at that time is carried out with a hydrogen-peroxide-solution solution, it is the value which measured with ion chromatography and was calculated, and most of the inorganic bromine gas is considered to be the hydrogen bromide which the bromine atom and hydrogen atom of a bromination polystyrene molecule ****, and is generated.

[0018] Moreover, the above-mentioned bromination polystyrene measures weight change before and after holding for 15 minutes at 300 degrees C, it is desirable that the value of the weight percentage reduction is 1.0 or less % of the weight, and it is more desirable that it is 0.5 or less % of the weight. It is bromination excellent in thermal stability in the value of weight percentage reduction being 1.0 or less % of the weight, and desirable.

[0019] As mentioned above, in manufacturing a bromination polystyrene particulate matter, it is possible to be a simple process and to collect bromination polystyrene particulate matters with saving resources and energy saving compared with the conventional recovery approach.

[0020]

[Example] Although an example is raised to below and this invention is explained in full detail, the range of this invention is not limited to these examples. In addition, measurement of the various properties in an example was performed by the following approaches.

[0021] (1) molecular weight -- using HPLC measuring device LC-10A (Shimadzu Make) equipped with GPC column KF[by - molecular-weight-distribution measurement Showa Denko K.K.]-805L, with steric exclusion

chromatography, number average molecular weight Mn and weight average molecular weight Mw were measured, and molecular weight distribution were computed from the formula of Mw/Mn. Measurement was proofread using standard polystyrene, using THF as an eluate.

[0022] (2) It dissolved in the tetrahydrofuran to which ethanol was added by making residual organic solvent ********** bromination polystyrene into an internal standard, and the amount of residual organic solvents was measured with the gas chromatography.

[0023] (3) Heat a bromine content sample with a fuming nitric acid in a well-closed container, it was made to decompose, and quantitative analysis of the generated hydrobromic acid was carried out using the approach (Carius method) of titrating with a silver nitrate.

[0024] (4) The 1.0g of the amount samples of generating inorganic bromines was heated for 10 minutes at 320 degrees C under the nitrogen air current at the time of heating, the trap of the part for the inorganic halogen in the gas which occurred was carried out with the hydrogen-peroxide-solution solution, and the quantum was carried out with ion chromatography (/MODEL 2000SP made from DIONEX).

[0025] (5) Hue (APHA)

The obtained bromination polystyrene was dissolved in the 50ml methylene chloride after 0.10g weighing capacity, and the hue of this solution was measured as compared with the HAZEN standard color solution. It is shown that a hue is so good that a value is small.

[0026] (6) After carrying out a temperature up from a room temperature to 300 degrees C using the thermogravimetric analysis equipment DuPont2000 by the TGA (heat weight) analysis tea ray instrument company with the programming rate of bottom 20 degrees C / of a nitrogen air current, and min, it held for 15 minutes and weight change of a sample in the meantime was measured.

[0027] After dichloromethane 89.7L and number average molecular weight added 15,000 and the molecular weight distribution added polystyrene 17kg of 2.5, and 0.45kg of aluminum chlorides to the reaction container in which 300L equipped with [example 1] stirring equipment, reflux equipment, and a thermometer carried out glass lining, 68.3kg of bromines was dropped over 1 hour so that internal temperature might maintain 5-15 degrees C. After ripening a reaction for after [dropping termination] 30 minutes, this reaction solution was rinsed. The dichloromethane solution (29.8-% of the weight concentration) of the bromination polystyrene after this rinsing was supplied to the heating tube (heat carrier; a steam, jacket temperature of 120 degrees C) of 5m of tube lengths by which the jacket heating was carried out in o'clock in 9kg /by bromination polystyrene conversion for the diameter of 13mm, and the uptake room (heat carrier; a steam, jacket temperature of 120 degrees C) which was maintained at degree of vacuum 200Torr and by which the jacket heating was carried out was made it to carry out a flash plate. The gage pressure of the heating tube at this time was 9kg/cm2. The bag filter (Hosokawa Micron Conex felt CF- 48 cel MEKKU processing) prepared in the uptake interior of a room separated the bromination polystyrene particulate matter and the dichloromethane steam, the capacitor with a brine temperature of -4 degrees C recovered dichloromethane, and after making a bromination polystyrene particulate matter pile up for 1 hour with the blender (jacket temperature of 100 degrees C) maintained at degree of vacuum 200Torr, it was taken out. The production process of this bromination polystyrene particulate matter was satisfactory even if it operated for about 5 consecutive hours. The amount of residual dichloromethanes of the bromine content of the obtained bromination polystyrene particulate matter was 50 ppm 67.3% of the weight. 15 and the hue of APHA are good, the inorganic bromine yield at the time of heating is 270 ppm, and the bromination polystyrene which 300 degrees C and whose weight percentage reduction for 15 minutes are 0.2 % of the weight, and was excellent in thermal stability was obtained.

[0028] After 1,2-dichloroethane 94.7L and number average molecular weight added 25,000 and the molecular weight distribution added polystyrene 17kg of 2.5, and 0.45kg of aluminum chlorides to the reaction container in which 300L equipped with [example 2] stirring equipment, reflux equipment, and a thermometer carried out glass lining, 68.3kg of bromines was dropped over 1 hour so that internal temperature might maintain 5-15 degrees C. After ripening a reaction for after [dropping termination] 30 minutes, this reaction solution was rinsed. The 1,2-dichloroethane solution (29.8-% of the weight concentration) of the bromination polystyrene after this rinsing was supplied to the heating tube (heat carrier; a steam, jacket temperature of 120 degrees C) of 5m of tube lengths by which the jacket heating was carried out in o'clock in 9kg /by bromination polystyrene conversion for the diameter of 13mm, and the uptake room (heat carrier; a steam, jacket temperature of 120 degrees C) which was maintained at degree of vacuum 200Torr and by which the jacket heating was carried out was made it to carry out a flash plate. The gage pressure of the heating tube at this time was 9kg/cm2. The bag filter (Hosokawa Micron Conex felt CF- 48 cel MEKKU processing) prepared in the uptake interior of a room separated the bromination polystyrene particulate matter and the 1,2-dichloroethane steam, the capacitor with a brine temperature of -4 degrees C recovered 1,2-dichloroethane, and

after making a bromination polystyrene particulate matter pile up for 1 hour with the blender (jacket temperature of 100 degrees C) maintained at degree of vacuum 200Torr, it was taken out. The production process of this bromination polystyrene particulate matter was satisfactory even if it operated for about 5 consecutive hours. The amount of residual 1,2-dichloroethane of the bromine content of the obtained bromination polystyrene particulate matter was 100 ppm 67.3% of the weight. 15 and the hue of APHA are good, the inorganic bromine yield at the time of heating is 280 ppm, and the bromination polystyrene which 300 degrees C and the weight percentage reduction for 15 minutes are 0.2 % of the weight, and was excellent in thermal stability was obtained.

[0029] After dichloromethane 89.7L and number average molecular weight added 5,000 and the molecular weight distribution added polystyrene 17kg of 2.0, and 0.45kg of aluminum chlorides to the reaction container in which 300L equipped with [example 1 of comparison] stirring equipment, reflux equipment, and a thermometer carried out glass lining, 68.3kg of bromines was dropped over 1 hour so that internal temperature might maintain 5-15 degrees C. After ripening a reaction for after [dropping termination] 30 minutes, this reaction solution was rinsed. The dichloromethane solution (29.8-% of the weight concentration) of the bromination polystyrene after this rinsing was supplied to the heating tube (heat carrier; a steam, jacket temperature of 120 degrees C) of 5m of tube lengths by which the jacket heating was carried out in o'clock in 9kg /by bromination polystyrene conversion for the diameter of 13mm, and the uptake room (heat carrier; a steam, jacket temperature of 120 degrees C) which was maintained at degree of vacuum 200Torr and by which the jacket heating was carried out was made it to carry out a flash plate. The gage pressure of the heating tube at this time was 9kg/cm2. The bag filter (Hosokawa Micron Conex felt CF- 48 cel MEKKU processing) prepared in the uptake interior of a room separated the bromination polystyrene particulate matter and the dichloromethane steam, the capacitor with a brine temperature of -4 degrees C recovered dichloromethane, and after making a bromination polystyrene particulate matter pile up for 1 hour with the blender (jacket temperature of 100 degrees C) maintained at degree of vacuum 200Torr, it was taken out. The obtained bromination polystyrene particulate matter shows high adhesiveness, and 2 hours after the blinding of a bag filter happening and beginning operation it not only adhering to a blender, but, it became impossible however, to operate it continuously. The amount of residual dichloromethanes of the bromine content of the obtained bromination polystyrene particulate matter was 200 ppm 67.2% of the weight. Moreover, the bromination polystyrene which 25 and a hue were a little inferior in APHA, and whose inorganic bromine yield at the time of heating is 500 ppm, and was inferior to 2 % of the weight and thermal stability in 300 degrees C and the weight percentage reduction for 15 minutes was obtained.

[0030] After 1,2-dichloroethane 94.7L and number average molecular weight added 8,000 and the molecular weight distribution added polystyrene 17kg of 1.9, and 0.45kg of aluminum chlorides to the reaction container in which 300L equipped with [example 2 of comparison] stirring equipment, reflux equipment, and a thermometer carried out glass lining, 68.3kg of bromines was dropped over 1 hour so that internal temperature might maintain 5-15 degrees C. After ripening a reaction for after [dropping termination] 30 minutes, this reaction solution was rinsed. The 1,2-dichloroethane solution (29.8-% of the weight concentration) of the bromination polystyrene after this rinsing was supplied to the heating tube (heat carrier; a steam, jacket temperature of 120 degrees C) of 5m of tube lengths by which the jacket heating was carried out in o'clock in 9kg /by bromination polystyrene conversion for the diameter of 13mm, and the uptake room (heat carrier; a steam, jacket temperature of 120 degrees C) which was maintained at degree of vacuum 200Torr and by which the jacket heating was carried out was made it to carry out a flash plate. The gage pressure of the heating tube at this time was 9kg/cm2. The bag filter (Hosokawa Micron Conex felt CF- 48 cel MEKKU processing) prepared in the uptake interior of a room separated the bromination polystyrene particulate matter and the 1,2-dichloroethane steam, the capacitor with a brine temperature of -4 degrees C recovered 1,2-dichloroethane, and after making a bromination polystyrene particulate matter pile up for 1 hour with the blender (jacket temperature of 100 degrees C) maintained at degree of vacuum 200Torr, it was taken out. The obtained bromination polystyrene particulate matter shows high adhesiveness, and 2 hours after the blinding of a bag filter happening and beginning operation it not only adhering to a blender, but, it became impossible however, to operate it continuously. The amount of residual 1,2-dichloroethane of the bromine content of the obtained bromination polystyrene particulate matter was 300 ppm 67.2% of the weight. Moreover, the bromination polystyrene to which 20 and the inorganic bromine yield at the time of heating are 350 ppm, and 300 degrees C and the weight percentage reduction for 15 minutes were inferior to 2 % of the weight and thermal stability in APHA was obtained.

[0031]

[Effect of the Invention] This invention is the approach of manufacturing a bromination polystyrene particulate matter, compared with the approach of adding the organic solvent solution of bromination polystyrene to a conventional non-solvent and a conventional boiling water, saving resources can be obtained at a simple process, few bromination polystyrene particulate matters of a residual organic solvent can be obtained with energy saving, and the industrial

effectiveness which does so is exceptional.

[Translation done.]